3.0 METHODS

This section describes the field and laboratory methods used to implement the 2014-2015 Monitoring Program.

In accordance with the 2012 Permit, the core monitoring program was conducted in compliance with the monitoring protocols set forth by the 2001 Permit's monitoring program. Collection and analysis of stormwater runoff during wet weather conditions and ambient (dry) weather runoff was performed at the MES in seven watersheds, Ballona Creek, Malibu Creek, Los Angeles River, Coyote Creek, San Gabriel River, Dominguez Channel, and Santa Clara River. Stormwater runoff during wet weather conditions and ambient (dry) weather runoff was also collected and monitored at six tributary locations within the Malibu Creek Watershed as described in Section 2.4.

The 2001 Permit's monitoring program requires sample collection at MES locations for a minimum of three storm events (including the first storm event of the season) and two dry events and at tributary stations for a minimum of four storm events (including the first storm event of the season) and one dry event. Under the 2001 Permit's monitoring program, tributary monitoring rotated between the seven watersheds. During the 2011-2012, 2012-2013, 2013-2014 and 2014-2015 monitoring years, tributary monitoring was conducted in the Malibu Creek Watershed. Stormwater samples and dry weather samples were analyzed for chemical constituents, indicator bacteria, and toxicity to bioassay test organisms (MES only).

Storm events at the Malibu Creek MES and Santa Clara River MES were monitored with the assistance of an environmental consulting firm, $WESTON^{\textcircled{\$}}$.

3.1 Precipitation and Flow Monitoring

3.1.1 Precipitation Monitoring

Precipitation monitoring was conducted at or near each MES using the various automatic rain gauges that LACFCD operates throughout Los Angeles County. A minimum of one automatic tipping bucket (intensity measuring) rain gauge was located nearby or within the tributary watershed for each MES. In some cases, large watersheds used multiple rain gauges to accurately characterize the rainfall. Existing gauges near the monitored watersheds were also used in stormwater runoff calculations and are essential in developing runoff characteristics for these watersheds.

3.1.2 Flow Monitoring

Because the 2001 Permit's monitoring program requires flow-weighted composites for many constituents, flow monitoring equipment was used to trigger the automated samplers. Flows were determined from water elevation measurements as described below.

The water elevation of an open channel was measured by the stage monitoring equipment, and the flow rate was derived from a previously established site-specific rating table or calculated with an equation (e.g., Manning's Equation). The LACFCD uses rating tables generated from

open channel, cross-section analysis and upstream/downstream flow characteristics. Previous flow measurement efforts indicated that all stations require multiple events to gather the data necessary for calibration of the measurement devices. The automatic samplers used pressure transducers as the stage measurement device. At the Santa Clara River MES, stadia rods were used to measure depth, and stream velocity was estimated by timing floating objects (leaf technique) as they traveled between rods set a fixed distance apart.

3.2 Wet Weather and Dry Weather Monitoring

During the 2014-2015 monitoring season, analyses of stormwater and dry weather samples consisted of field measurements, grab samples, and composite samples in accordance with the methods described below. A field log was completed at each site for each event. The field log sheets included empirical observations of the site and water quality characteristics.

3.2.1 Wet Weather Sample Collection Methods

Field Measurements – Field measurements, which included pH, dissolved oxygen (DO), conductivity, turbidity, and temperature, were conducted using a calibrated YSI (or similar meter) at the Malibu and Santa Clara River MES. Meters were allowed to stabilize for one minute prior to recording readings. Operation of meters was conducted as per manufacturer instructions, and meters were calibrated per manufacturer specifications within one week prior to use to ensure accurate functionality.

Photographic Trash Surveys - Trash monitoring was conducted to assess the quantities of trash in receiving waters after storm events and to identify areas impaired for trash. Visual observations of trash were made and photographs were taken at the MES locations after four storm events (three at Santa Clara MES), including the first flush.

Grab Sample - A grab sample is a discrete, individual sample taken within a short period of time, usually less than 15 minutes. This method is used to collect samples for constituents not amenable to composite sampling due to short holding times and specific collection or preservation needs. Grab samples were analyzed for indicator bacteria and for conventional pollutants, as shown in the table below.

Grab Sample Constituents	
Conventional Constituents/Parameters	Indicator Bacteria
 Oil & grease Total phenols Cyanide Dissolved oxygen (DO) Total petroleum hydrocarbons (TPH) Methyl tertiary butyl ether (MTBE) 2-Chloroethyl vinyl ether 	 Total coliforms Fecal coliforms Fecal streptococci Fecal enterococci E. coli

Analytical methods, method detection limits (MDLs), and holding times for these constituents are provided in Table 3-1.

Grab samples were collected during the initial portion of the storm event (i.e., on the rising limb of the hydrograph), placed on ice, and taken directly to the laboratory. Samples were collected from the horizontal and vertical center of the channel if possible and kept clear from uncharacteristic floating debris. Because oil and grease and other petroleum hydrocarbons tend to float, oil and grease grab samples were collected at the air—water interface unless flows did not allow for the safe collection of samples. In these cases, grab samples were collected using the automated samplers. Bacteria samples were collected in a sterile sample bottle and then placed on ice for transport to the laboratory for analysis within 8 hours of collection

Composite Sample - A composite sample is a sample created by combining a series of discrete samples (aliquots) of specific volume, collected at specific flow-volume intervals. Composite sampling is ideally conducted over the duration of the storm or other monitoring event. Composite samples were analyzed for conventional constituents, general minerals, pH, nutrients, metals, semivolatile organics, base neutral, chlorinated pesticides, PCBs, organophosphate pesticides, and herbicides. Samples from the MES were also analyzed for toxicity, which is described in detail in Section 3.3.3. In addition, all storm events resulting in at least 0.25 inch of rainfall were monitored for TSS at all MES equipped with automated samplers. Per the 2001 Permit, this additional TSS analysis was not conducted where manual sampling was required (i.e., Santa Clara River MES). In addition, TSS was not analyzed at the Los Angeles River MES during 2014-15Event08 due to equipment failure. Telemetry will be installed at all automated MES for the 2015-16 storm season to improve responsiveness to equipment failures and ensure collection of all required storm events. New auxiliary pumps will also be installed at all automated MES to prevent future equipment malfunctions.

Composite Sample Constituents	
 General pH Nutrients Metals Semivolatile organics Base/neutral 	 Chlorinated pesticides Polychlorinated biphenyls Organophosphate pesticides Herbicides Toxicity

Specific composite analytes, analytical methods, MDLs, and holding times for these constituents are provided in Table 3-1.

Most flow-weighted composite storm samples were obtained using an automated sampler programmed to collect samples at flow-paced intervals. Since an automated sampler has not yet been installed at the Santa Clara River MES, composite samples were obtained at this location by sampling discretely from the river at 20-minute intervals for the first three hours of the storm (or the duration of the storm if it was less than three hours). The discrete samples were then combined in the laboratory in proportion to the estimated flow rates (i.e., a flow-weighted composite).

During the storm season, the automated samplers were programmed to start automatically when the water level in the channel or storm drain exceeded a minimum predetermined level above base flow or prevailing pre-storm flow. Some MES also use an automatic tipping bucket rain gauge installed at the station to start the automated sampler program only when storm flow and rainfall exceed established thresholds. These practices were developed based on years of monitoring experience in local watersheds. It was particularly useful when automated samplers needed to be reset to capture storms occurring a little over 24 hours apart and it was not possible to wait for flows to return to base flow conditions.

A sample was collected each time a set volume of water had passed the monitoring point. This volume is referred to as the pacing volume or trigger volume. Samples were stored in 2.5-gallon glass containers within the sampler. An 8-liter minimum sample volume was required to conduct the necessary laboratory analyses. The automated sampler was deactivated by field personnel within 24 hours after the end of each storm event. Samples were retrieved from the automated samplers as soon as possible to meet laboratory analysis holding time requirements. As samples were collected, rainfall, discrete sample times and runoff data were logged and stored for transfer to the office. For TSS only sampling events, sample bottles were collected about 48-hours after the end of each storm event as this was permissible due to the 7-day holding time for TSS. Samples were only collected while flows remained above an established threshold.

3.2.2 Dry Weather Sample Collection Methods

Dry weather monitoring protocols were similar to those used for wet weather monitoring.

Grab samples were collected and analyzed for the constituents identified in Section 3.2.1. During dry weather sampling for the MES with automated samplers, composite samples were collected as time-weighted composites over a 24-hour period, and automated samplers were programmed to start at a specified time. Santa Clara River MES composite samples were obtained by sampling discretely from the river at 20-minute intervals for three hours. Composite samples were analyzed for the constituents identified in Section 3.2.1.

3.2.3 Field Quality Assurance / Quality Control

Quality assurance (QA)/quality control (QC) is an essential component of the monitoring program. *Evaluation of Analytes and QA/QC Specifications for Monitoring Program* (Woodward-Clyde, 1996) describes the procedures used for bottle labeling, chain-of-custody (COC) tracking, sampling equipment checkout and setup, sample collection, field blanks to assess field contamination, field duplicate samples, and transportation to the laboratory.

An important part of the QA/QC plan is the continued education of field personnel. Field personnel were trained from the onset and were informed regarding new or revised stormwater sampling techniques on a continual basis. Field personnel also evaluated the field activities required by the QA/QC plan, and the plan was updated if necessary. Accurate data were obtained by proper monitoring station setup, water sample collection, sample transport, and laboratory analyses.

QA/QC for sampling processes included proper collection of the samples to minimize the possibility of contamination. Samples were collected in clean sample bottles, sterilized by the laboratory. Sampling personnel were trained according to the field sampling SOPs. Additionally, the field staff was made aware of the significance of the project's detection limits and the requirement to avoid contamination of samples.

Field parameters were measured and recorded at Malibu Creek MES and Santa Clara River MES using the appropriate calibrated equipment and were reviewed immediately using best professional judgment to ensure accurate measurement of parameters.

3.2.3.1 Field Setup Procedures

Automated field sampling stations were at fixed locations, with the sampler placed on a public road right-of-way or flood control easement. Inspection of visible hoses and cables was performed to ensure proper working conditions according to the station design. Inspection of the intake tube, pressure transducer, and auxiliary pump was performed during daylight hours in normal (i.e., non-storm) conditions.

For stormwater sample collection, the automated samplers were programmed prior to the event based upon weather forecast information. The automated samplers were checked at the beginning of the storm to ensure proper working conditions and to determine whether flow composite samples were being collected properly. Grab samples were taken during the rising limb of the hydrograph where feasible.

For dry weather, following the initial grab sample collection, field staff prepared the sampler to collect subsequent time-weighted composite samples until the entire set had been completed for that station. Dry weather collection techniques were similarly performed for both grab samples and 24-hour composite samples.

When a complete set of samples had been collected for a given event, the bottles were removed from the sampler, labeled, and packed with ice and foam insulation inside individually marked ice chests. COC forms were completed by field staff before transporting the samples to the laboratory. Under no circumstances were samples removed from the ice chest during transportation from the field to the laboratory.

3.2.3.2 Bottle Preparation

A minimum of two sets of bottles were prepared for each monitoring station so that change-outs could be made quickly between closely occurring storms. Bottle labels included the following information:

- LACFCD's Field Sample Identification (FSID) number.
- Station (site) number.
- Station (site) name.
- Laboratory analysis requested.
- Date (written at time of sampling).
- Sampler name: Los Angeles County Department of Public Works, Watershed Management Division

Bottles were cleaned at the laboratory prior to use, labeled, and stored in sets. Each station was provided with the same number, type, and size bottles for each rotation, unless special grab samples were required. Clean composite sample bottles were placed in the automated sampler when samples were collected. This practice ensured readiness for the next storm event. All bottles not in use at the time of sampling were stored in clean dry conditions for later use. Composite sample bottles were limited to a maximum of 2.5 gallons each, to ensure ease of handling.

3.2.3.3 Chain-of-Custody Procedure

COC procedures (Woodward-Clyde, 1996) were used for all samples throughout the collection, transport, and analytical process. Samples were considered to be in custody if they were: (1) in the custodian's possession or view (2) retained in a secured place (under lock) with restricted access, or (3) placed in a container and secured with an official seal to prevent the sample from being reached without breaking the seal. COC records, field logbooks, and field tracking forms were the principal documents used to identify samples and to document possession. The COC procedures were initiated during sample collection. A COC record was provided with each sample or group of samples. Each person with sample custody signed the form and ensured the samples were not left unattended unless properly secured. Documentation of sample handling and custody included the following:

- Project name and the company name and address
- Bottle label information (i.e., the LACFCD FSID number, station (site) number, station (site) name, laboratory analyses requested, and date (written at time of sampling)).
- Time (written at time of sampling).
- Number of bottles.
- Temperature of sample.
- Sampler(s), laboratory and sampler/courier signatures, and time(s) sample(s) changed possession (completed upon sample transfer(s)), including total number of containers received and sample condition at receipt.
- Check box for "Hold Analysis" or "Final Samples".
- Comments.

3.2.3.4 New Zealand Mud Snails

Due to concern about the spread of non-native New Zealand Mud Snails, additional decontamination of monitoring equipment between Malibu MES and tributary monitoring stations was conducted. A designated set of sampling equipment (exclusive of temperature and pH field meters) was used for each of the stations in the Malibu watershed (Malibu MES and tributary stations), and was decontaminated before and after each event. Decontamination procedures as described by the California Department of Fish and Game (Hosea and Finlayson, 2005) were employed and included immersion of sampling equipment in Sparquat 256.

Field meters utilize sensitive osmotic membranes for use in measurement of pH. Therefore, the use of freezing or Sparquat 256 as a decontamination method was not employed. Field meters were visually inspected after use at each location; and all snails, mud, algae, and debris were

removed. The meters were then thoroughly rinsed on-site with tap water and allowed to dry completely. Visual inspection of the field meters was completed prior to departure from the station and before use at the next monitoring location.

3.3 Laboratory Analyses

The chemical and toxicological analyses conducted during the 2014-2015 monitoring year are described in the following sections.

3.3.1 Laboratory Background and QA/QC

The Los Angeles County Department of Agricultural Commissioner Weights and Measures (ACWM) Environmental Toxicology Laboratory provides water quality laboratory and related services to LACFCD. The ACWM Laboratory is state certified to perform water quality analyses and maintains a laboratory analysis program and quality assurance manual with quality QA/QC protocols consistent with the monitoring program.

The ACWM subcontracts toxicity testing with Aquatic Bioassay Consulting Laboratories, Inc. (ABC) of Ventura, California. This laboratory is accredited by the State of California's Environmental Laboratory Accreditation Program (ELAP; certificate number 1907) for whole effluent toxicity of wastewater testing as well as for other types of analyses. Analyses were conducted in accordance with procedures set forth in the laboratory's QA/QC manual.

The QA/QC objectives for the chemical and toxicological analyses conducted by the participating analytical laboratories are detailed in their Laboratory QA Manuals. The objectives for accuracy and precision involve all aspects of the testing process, including the following:

- Methods and SOPs
- Calibration methods and frequency
- Data analysis, validation, and reporting
- Preventative maintenance
- Internal QC
- Procedures to ensure data accuracy and completeness

QC samples that failed to meet the specified QC criteria in the methodology were identified, and the corresponding data qualified.

A review of the 2014-2015 reported results for dissolved metals identified certain anomalies that were investigated. Should these anomalies arise again during the 2015-2016 monitoring period, a further investigation may be conducted, the results of which would be provided in next year's report, as appropriate.

3.3.2 Chemical and Biological Analyses

The 2001 Permit specified a suite of analyses and associated minimum levels (MLs) for samples collected at the MES and tributary locations, as detailed in Table 3-1. The laboratory methods used for analyzing stormwater samples are approved by the California Department of Public

Health (CDPH) and conform to United States Environmental Protection Agency (EPA)-approved methods.

3.3.3 Toxicity Analysis

Toxicity testing was performed on flow-weighted composite samples collected from the MES locations concurrently with the water chemistry analyses during two wet weather events. Toxicity testing was also performed on time-weighted composite samples during two dry weather events at the MES locations.

Toxicity testing is an effective tool for assessing the potential impact of complex mixtures of unknown pollutants on aquatic life in receiving waters. Rather than performing chemical analysis on a sample for a host of compounds potentially toxic to aquatic life, toxicity testing provides a direct measure of the toxicity of the sample to laboratory test organisms. Interactions among the complex mixture of chemicals and physical constituents inherent to environmental samples can lead to additive or antagonistic effects, potentially causing an individual compound to become either more or less toxic than it would be if it were isolated. Although the potential effects of these interactions cannot be derived from simple chemical measurements, they are directly accounted for in toxicity tests. If toxicity is identified in a given sample, toxicity identification evaluations (TIEs) may be used to help characterize and identify the constituent(s) causing or contributing to the observed toxicity. Toxicity testing can provide information on both potential short-term (i.e., acute) effects as well as longer-term (i.e., chronic) effects.

Toxicity analysis was performed using the following methods:

- Ceriodaphnia dubia 7-day (chronic) survival and reproduction tests.
- Strongylocentrotus purpuratus (sea urchin) (chronic) fertilization test.

The tests were performed using multiple sample concentrations ranging from 0 percent (%) (N-control) to 100%, such that the desired toxicity endpoints could be adequately observed. Based on the endpoints of reproduction and survival, the no-observed-effect concentrations (NOEC), inhibitory concentrations (IC), effective concentrations (EC), and toxicity units (TU) were calculated and reported for each test. Toxicity units are calculated by dividing 100 by the calculated median test response value (e.g., IC₅₀), per the 2001 Permit's monitoring program. The *C. dubia* and *S. purpuratus* tests were conducted under guidelines prescribed in *Short-Term Methods for Estimating the Chronic Toxicity of Effluents and Receiving Waters to Freshwater Organisms* (EPA, 2002) and *Short-Term Methods for Estimating the Chronic Toxicity of Effluents and Receiving Waters to West Coast Marine and Estuarine Organisms* (EPA, 1995), respectively. Water quality measurements (i.e., temperature, pH, DO, conductivity, salinity, hardness, and alkalinity) were recorded for each sample at the beginning and throughout each test. These measurements were performed to ensure that there were no large variations in water quality, which can affect the accuracy of the toxicity tests.

3.3.3.1 2012 Permit Toxicity Analysis

In accordance with the 2012 Permit, the core monitoring program was conducted during 2014-2015 in compliance with the monitoring protocols set forth by the 2001 Permit's monitoring program. Monitoring will be conducted under the CIMPs, once they are approved by the Regional Board, and will include updated toxicity testing requirements in the 2012 Permit monitoring program.